

Halogen Sources and their Influence on Winter Air Pollution in the Great Salt Lake Basin

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1. Scope of Work

1.1 Abstract

The Great Salt Lake Basin is meteorologically and chemically distinct from other regions in the U.S. It is subject to both persistent cold air pools in complex terrain that lead to winter air pollution and potentially large inputs of natural and anthropogenic sources of halogen species. Here we propose to investigate the role of these halogen sources in regulating the severity of winter PM_{2.5}. Aircraft and ground-based measurements from the 2017 Utah Winter Fine Particulate Study (UWFPS) provided state of the art measurements of speciated halogens, including the di-halogens (Cl₂, Br₂, etc.), nitryl halides (ClNO₂) and hydrochloric acid (HCl), among others. We propose a two-part analysis to leverage these unique measurements. The first phase will investigate the magnitude of industrial emissions of chlorine and bromine to better constrain emissions inventories for these species. These emissions play a direct role in PM_{2.5} formation through gas-particle partitioning of chloride. They also play an indirect role in PM_{2.5} formation through the production of atmospheric radicals, which in turn drive oxidation cycles that lead to PM_{2.5}. The second phase will assess the role of halogen emissions on ozone and other oxidants in the region adjacent to industrial facilities on the west shore of the Great Salt Lake, and more broadly across the Great Salt Lake and adjacent valleys. The goal of this analysis is to determine if there is a widespread effect of halogens on ozone, and if so, its influence on winter PM_{2.5}, which itself is dependent on ozone.

The proposal is responsive to the goals and priorities of the UDAQ Science for Solutions program in the following areas.

- Emissions Inventory Improvements
 - Halogen emission rate estimates for the Wasatch Front region
- PM_{2.5} Formation and Precursor Gases
 - Halogens
 - Oxidized nitrogen compounds
 - Atmospheric radicals
- PM_{2.5} Chemical Composition and Sources
 - Particulate chloride sources

The PIs for this proposal are from NOAA and its joint institute with the University of Colorado. These investigators led the measurements and analysis from UWFPS 2017. The proposal includes in-kind contribution from NOAA in the commitment of the principal investigator's time at no cost. This analysis would not be easily supported absent funding from UDAQ.

1.2 Basis and Rationale

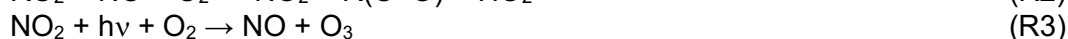
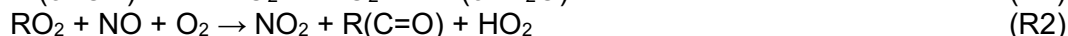
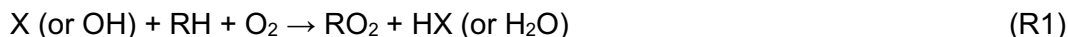
The airsheds of the Great Salt Lake Basin are unique compared to other inland areas in that they consist of a combination of urban and rural mountain valleys with complex topography, and in that these regions are subject to both natural and anthropogenic sources of airborne halogen species (Cl, Br, I). The complex terrain is one of the key factors that makes the region sensitive to the buildup of air pollution during the winter season, when meteorological inversions below the height of the surrounding terrain trap surface emissions within the valleys [1]. These events

are known as persistent cold air pools, PCAPs, and are associated with high levels of particulate matter with diameter smaller than 2.5 microns, $PM_{2.5}$, which frequently exceed regulatory limits [2-4]. Halogens are chemically reactive species that may contribute to the cycles that produce $PM_{2.5}$ in the region. Relevant sources of halogens may include, but are not limited to, spray from the Great Salt Lake, playa dusts from salt beds, industrial processes such as the production of magnesium and chlorine, the application of road salt during the winter season, and emissions from combustion.

Halogens drive a number of chemical cycles that have the potential to affect regional air quality [5, 6]. Photolysis of stable halogen compounds, Cl_2 , Br_2 , $BrCl$, $ClNO_2$, etc., is a source of halogen radicals, Cl , ClO , etc. These radicals affect both the photochemical production and destruction of ozone, the oxidation rates of volatile organic compounds (VOCs) and the subsequent production of peroxy radicals that are key components of ozone production reactions and cycles that produce ammonium nitrate aerosol. They enter into both radical propagation and termination cycles involving HO_x ($=OH + NO_2$) and NO_x ($=NO + NO_2$), thus affecting radical sources and budgets. They may also undergo heterogeneous recycling reactions that serve to propagate halogen driven atmospheric chemical cycles [7, 8]. Therefore, a better understanding of the halogen cycles is key to developing a fuller picture of air quality in the Great Salt Lake Basin.

1.2.1 Halogen Cycles Relevant to Utah Air Quality

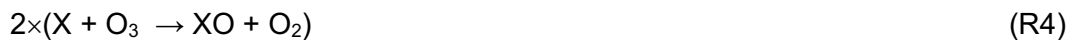
Perhaps the most important cycles involving halogens are those that regulate the ozone budget. Previous work on halogen cycles in areas subject to regional air pollution have focused on their role as an ozone source [9, 10] through oxidation of VOCs in a high- NO_x environment.



Here X is a halogen radical (and OH is the hydroxyl radical), RH refers to a hydrocarbon (VOC), RO_2 is an organic peroxy radical, $R(C=O)$ is a carbonyl compound, and (R3) represents photolysis of NO_2 leading to atomic oxygen that combines with O_2 to produce ozone. Reaction (R1) proceeds primarily by hydrogen abstraction and is typically very rapid if $X=Cl$. It can be important if the primary source of the atomic halogen radical (X) from photolysis of stable halogens is significant in comparison to other primary radical sources [11]. If Cl -driven VOC oxidation is appreciable relative to OH , it changes the overall reactivity of VOCs that participate in ozone formation, since Cl reaction rate constants are rapid with species such as alkanes that react slowly with OH . Thus, quantifying the sources of halogens in general, and Cl in particular, can be important for understanding regional air quality.

The major component of winter air pollution in the Great Salt Lake basin is ammonium nitrate aerosol, which is associated with low levels of ozone. However, recent analysis of the chemical cycles that lead to ammonium nitrate have shown that they are equivalent to those that produce ozone during summer, and that reactions (R1-R3) are essential components of this cycle [12]. Furthermore, during the winter, primary sources of OH radicals tend to be considerably smaller due in part to reduced photolysis of common HO_x ($=OH + HO_2$) precursors. Thus, there is potential for halogens to play a greater role in oxidation cycles during winter. Because the Great Salt Lake basin is subject to potentially larger sources of halogens than other regions, its sensitivity to these sources is greater. Quantifying the sources and their role in regional atmospheric chemistry may therefore be important to modeling wintertime $PM_{2.5}$ pollution.

A second halogen cycle that affects ozone is the catalytic destruction cycle that is initiated by the reaction of an atomic halogen radical with ozone.



This cycle is important in the case where the $X + O_3$ reaction (R4) is competitive with $X + RH$ (R1). The cycle is well known as one of a number of ozone destruction cycles that affect the stratospheric ozone layer and that are thought to be responsible for tropospheric ozone depletion observed in the arctic [8]. There are only two instances in which halogen-driven ozone destruction has been observed in the troposphere at mid-latitudes, and one of those regions is the Great Salt Lake Basin. Stutz *et al.* [13] report long-path, spectroscopic observations of halogen oxide radicals from a site in the Salt Lake Valley to the west of Salt Lake City and slightly south of the Great Salt Lake shoreline in October of 2000. The observations of ClO and BrO at a few part per trillion by volume (pptv) mixing ratios were associated with reductions in ozone levels below the ambient background. Ambient levels of NO_x , which are also known to affect ozone, were too low to be responsible for the observed ozone change.

Industrial facilities located on the west shoreline of the Great Salt Lake are a known source of halogens. This was ruled out as a source of the observed halogen oxide radicals and ozone depletion in Stutz *et al.* [13] on the basis of simultaneous observations of low NO_2 , which also originates in this region, and back-trajectory calculations that passed over the playas of the neighboring Tooele Valley rather than the industrial areas of the western Great Salt Lake. The observation implies that natural sources of halogens, activated through heterogeneous reactions of halide salts, may be important to the ozone and oxidant budgets in the Great Salt Lake region. However, measurements from the recent UWFPS campaign (described in the next section), unmistakably detected ozone depletions in plumes from the plant. The only other published observation of mid-latitude tropospheric ozone destruction attributable to halogen reactions occurred in the Dead Sea region [14], an area geographically similar to the Great Salt Lake.

A third relevant halogen cycle is the heterogeneous uptake of dinitrogen pentoxide, N_2O_5 , on chloride containing aerosol (or deposition of N_2O_5 to surfaces) leading to the production of nitryl chloride, $ClNO_2$ [15, 16].



Reactions (R7-R9) are relevant mainly at night due to the photochemical instability of the nitrate radical precursor, NO_3 , in reaction (R7). The symbol ϕ varies between 0 – 1 and indicates the yield of $ClNO_2$ from the heterogeneous uptake of N_2O_5 . The aerosol in (R9) contains both liquid water, H_2O , which leads to $2HNO_3$ if it is the reaction partner for N_2O_5 , and chloride (Cl^-), which leads to $ClNO_2 + HNO_3$. Photolysis of $ClNO_2$ on the following day is a source of atomic Cl that can participate in the cycles above.



The efficiency of this cycle has been analyzed in a recent manuscript from UWFPS [17]. Its role in regional air quality has been analyzed in detail in other regions during both the summer and winter seasons [18-20]. In the Great Salt Lake Basin, it has two major effects. The first is to reduce the role of nighttime heterogeneous uptake of N_2O_5 in producing soluble nitrate (HNO_3 or particulate nitrate, pNO_3^-), one of the major pathways leading to the production of ammonium nitrate aerosol. The second is to provide a radical or oxidant source through reaction (R10). This radical source, in turn, enhances the daytime oxidation of NO_x into soluble nitrate, thereby further contributing to a major component of wintertime $\text{PM}_{2.5}$ formation [11, 21]. The cycle depends critically on the availability and partitioning of soluble chloride (HCl + particulate chloride, pCl^-).

Finally, halide salts, particularly chloride, may make a non-negligible contribution to winter $\text{PM}_{2.5}$ through the reversible reaction with ammonia to form ammonium chloride.



Kelley *et al.* [22] inferred a relatively large contribution, up to 15%, of NH_4Cl to total $\text{PM}_{2.5}$ mass in their analysis of air quality data from three sites along the Wasatch Front. They assessed the most-likely source of this chloride to emissions from industrial emissions. If so, this single halogen emission source has an outsized impact on winter air quality in the region, a hypothesis that requires further investigation. Franchin *et al.*, [23] in their recent analysis of aircraft data across the Great Salt Lake Basin, find a smaller overall contribution of pCl^- to total $\text{PM}_{2.5}$ mass of 2% on average, but nevertheless find pCl^- to be a ubiquitous component of particulate mass across the entire region and to represent as much as 20% of aerosol mass in individual measurements.

Because of the direct role of halogens in multiple atmospheric chemical processes that affect winter air quality across the Great Salt Lake Basin, quantitative assessment of their abundance, speciation, sources and atmospheric chemistry is an essential input to models that are used for assessment of winter $\text{PM}_{2.5}$ and its mitigation in the region.

1.2.2 The 2017 Utah Winter Fine Particulate Study

The 2017 Utah Winter Fine Particulate Study (UWFPS) was an aircraft and ground based field study that collected one of the most comprehensive data sets to investigate winter air quality in the Great Salt Lake Basin [24].

The NOAA Twin Otter is a light aircraft that surveyed the spatial distribution, both vertical and horizontal, of key air pollutants. It executed 23 research flights between January 16 and February 23 across several air basins. Its payload was targeted towards trace gases and aerosols thought to be most important in the formation of ammonium nitrate and other components of winter $\text{PM}_{2.5}$. These included high precision, fast time response nitrogen oxides (NO , NO_2) and ozone (O_3) from a custom built cavity ring-down spectrometer, speciated aerosol composition from an Aerosol Mass Spectrometer (AMS), ammonia (NH_3) from a fast time response tunable diode laser spectrometer, and acid gases such as nitric acid (HNO_3) and hydrochloric acid (HCl) from a state-of-the art, high precision, fast time response mass spectrometer (iodide ion, time of flight chemical ionization mass spectrometer, I- ToF CIMS). Importantly, the I- ToF CIMS also reported several speciated halogen compounds, including molecular halogens (Cl_2 , Br_2 , BrCl), nitryl halides (ClNO_2 , BrNO_2) and hypohalous acids (HOCl

and HOBr). The I-ToF CIMS instruments were directly calibrated to most of these gas-phase reactive halogen species in the field or just before or after the UWFPS campaign.

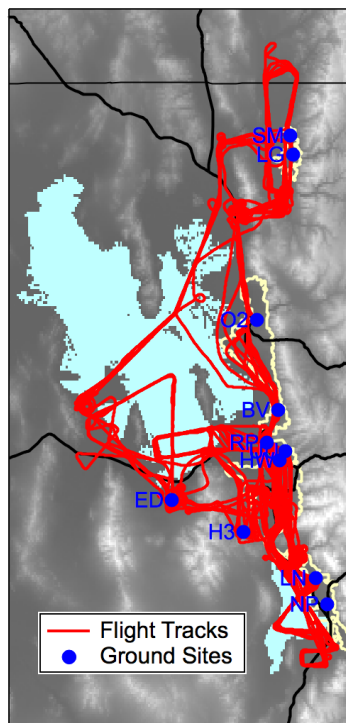


Figure 1: Twin Otter flight tracks and ground sites during UWFPS 2017 in the Great Salt Lake region.

A ground site in Logan, Utah, in the Cache Valley, operated by the EPA, incorporated a similar set of measurements, also employing an AMS, an I-ToF CIMS, gas phase ammonia measurement, and instrumentation for NO_x and O_3 , among others. A ground site at the University of Utah also included measurements of gas and particulate phase reduced and oxidized nitrogen, albeit with different instrumentation than on the Twin Otter or at the Logan – Cache Valley site. Additional sites across the region, such as Hawthorne in the Salt Lake Valley and Lindon in the Utah Valley (Lindon) provided more routine monitoring data. Figure 1 shows the flight tracks of the NOAA Twin Otter superimposed on the ground sites.

The suite of measurements from the Twin Otter, which included gas and particulate phase acid base pairs, such as $\text{HNO}_3 + \text{pNO}_3^-$, $\text{HCl} + \text{pCl}^-$, $\text{NH}_3 + \text{pNH}_4^+$, has already been used in an analysis of the distribution of these trace gases and aerosol components and the sensitivity of winter $\text{PM}_{2.5}$ to reductions in total oxidized ($\text{HNO}_3 + \text{pNO}_3^-$) and reduced ($\text{NH}_3 + \text{pNH}_4^+$) nitrogen [23]. A recent analysis

has assessed the efficiency of nighttime ClNO_2 production through reaction (R9) [17].

The halogen data collected by the instruments suggests a significant role for these species in winter air chemistry. Both chlorine and bromine compounds were ubiquitous over the region at levels often as high as coastal urban areas. Industrial activities are a substantial direct anthropogenic source of these halogens. We observed multiple events where boundary layer ozone is significantly reduced or even depleted to levels below detection limits of the aircraft instrument and that correspond in space and time to elevated reactive halogen species. Similarly, we observe significant contributions of aerosol chloride to $\text{PM}_{2.5}$ as well as ClNO_2 , a source of radicals for daytime photochemical production of secondary pollutants such as ozone and nitrate. These aspects of the halogen measurements require further analysis to quantify their role and to make best use of the UWFPS data set.

1.3 Technical Approach

We propose further analysis of two aspects of the UWFPS halogen measurements. The first is to describe the abundance, distribution and speciation of halogens and halides in the Great Salt Lake Basin and quantify their major natural and anthropogenic sources. This analysis will look specifically at industrial emission sources on the west side of the Great Salt Lake, as well as the broad halogen activation cycles outlined above. The second analysis is to examine the impact of halogens on ozone and odd oxygen budgets in the region. The observation of ozone depletion events associated with the presence of halogens appears to be a unique feature of this region, and has not been reported in other polluted airsheds in North America. The goal of this effort will be to use the unique observations from UWFPS to assess the current level of understanding of halogen chemistry and cycling. A second goal will be to determine the impact

of this atmospheric chemistry on the oxidation capacity of polluted boundary layers associated with PCAP events in the region, which in turn affect the rates of accumulation of $PM_{2.5}$.

1.3.1 Halogens in the Great Salt Lake Basin

Halogen species are present in different forms across the Great Salt Lake basin, as Figure 2 illustrates. Here, we propose an analysis to (i) evaluate the regional importance of these industrial halogen sources against those of the Great Salt Lake and surrounding playa dusts, (ii) evaluate the distribution of gas and aerosol phase chloride throughout the region, and (iii) compare the importance of photo-labile halogen atom precursors such as Cl_2 and $ClNO_2$ to other photochemical radical sources in the region.

Question 1. What are the natural and industrial sources, and spatial and temporal distribution, of key reactive halogen species (HCl , Cl_2 , particulate chloride, $ClNO_2$, Br_2 , $BrCl$, etc) in the Great Salt Lake Basin?

Analysis Method: Plume analyses to determine emission factors of halogen species from industrial sources and analysis of fluxes through other halogen activation mechanisms on a regional basis.

1.3.1a Industrial Halogens

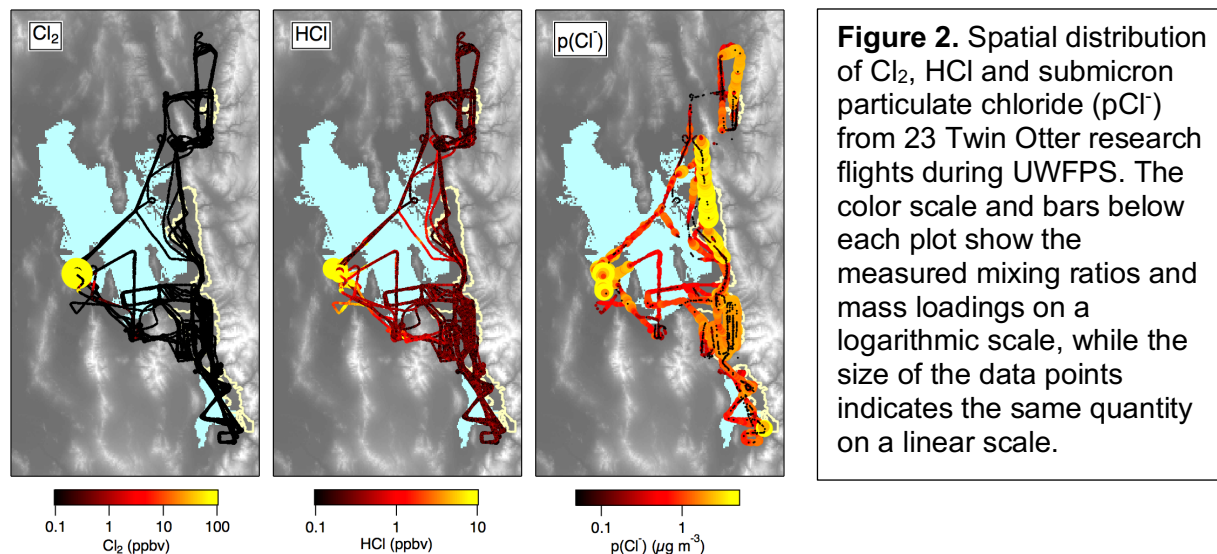
As noted in the UWFPS report [24], an industrial facility is located on the western edge of Stansbury Bay of the Great Salt Lake, due west of the northern tip of Stansbury Island. On several Twin Otter flights, a plume rich in halogens was detected at and just downwind of this facility. Mixing ratios of Cl_2 were often very large, sometimes in excess of 100 ppbv, although the color scale in the left panel of Figure 2 saturates at this level. Little Cl_2 was present elsewhere in the basin. Other di-halogen species were also observed. Br_2 ranged from ~ 1 to >10 ppb, and $BrCl$ mixing ratios were often in between those of Br_2 and Cl_2 . These are some of the highest mixing ratios of di-halogens ever measured in ambient air.

There are two other smaller but detectable point sources in the Utah Valley that show elevated Cl_2 . One of these is located on the northeast edge of Utah Lake, where there was also a natural gas power generation unit and a fertilizer plant. The co-enhancement of NO suggests a co-located combustion source, but whether the Cl_2 was from one of those or a different, co-located source is not yet clear. The other source is located to the southeast of Utah Lake, near the Spanish Fork area.

We propose to analyze the Twin Otter measurements of reactive halogens, NO_x and other trace gases to determine the emission ratio (e.g., relative to NO_x) of a suite of halogens from industrial point sources. From the emission ratio determined from Twin Otter measurements and independently measured emission rates of NO_x and other gases from reported point source emissions, we will obtain the emission rates of speciated halogens. This total emission rate can be compared to the existing inventory, which does not speciate into different forms of reactive halogens, and which has not been validated from direct airborne observations before. We will be able to report emission rates of both chlorine and bromine species. Bromine emissions have a more potent effect, per mole, on ozone abundance as described below.

In addition, we will utilize on-board measurements of meteorology to provide an estimate of the emission rates by conducting a flux analysis. In this approach, we use the measured vertical profile of horizontal windspeed and the integral of halogen concentration enhancements across

a horizontal transect to derive an emission flux from the industrial source. This is a standard approach for measuring emission fluxes downwind of point sources that has been applied to the analysis of emissions of other trace gases [25-27]. The ratios of the emission fluxes from this method can then be compared to the inventories as well.



1.3.1b Gas and particulate phase chloride and ClNO_2

Figure 2 shows that HCl was elevated near the industrial di-halogen source on the west side of the Great Salt Lake, but that it was also more widespread throughout the region. Distinct, sharp HCl plumes exceeded 100 ppbv on several intercepts, although the color scale in Figure 2 saturates at 10 ppbv to show the broader distribution of HCl. The more uniform distribution of HCl is likely due in part due to its longer atmospheric lifetime, its secondary production from photolysis of other chlorine reservoirs such as Cl_2 and ClNO_2 , and potentially from more distributed sources. HCl is also in thermodynamic equilibrium with particulate chloride, pCl^- , which Figure 2 shows to have an even more widespread regional distribution. Analysis of the vertical and horizontal distribution of these chloride species and their correlations with other trace gases will provide an indication of the major source for these species from industrial, natural, urban or other source categories. Quantitative analysis of all chloride sources may be difficult and / or limited with the available aircraft data from UWFPS, but the goal will be to determine as much as possible to within the constraints of the data set on the role of industrial chlorine sources relative to the total. The industrial source has been inferred as a large contributor to particulate chloride from previous analyses [22].

Soluble chloride ($\text{HCl} + \text{pCl}^-$) provides a source of photolabile chlorine that affects oxidant budgets through the ClNO_2 cycle in reactions (R7-R10). Our previous analysis of UWFPS data quantified the yields of ClNO_2 (ϕ) on ambient $\text{PM}_{2.5}$ in the region [17]. We propose here to quantify the photolysis of ClNO_2 as a source of regional oxidant. This budget can be developed from the ClNO_2 abundances during both clean and polluted periods, as well as from the amount of NO_x and the efficiency with which NO_x cycles through ClNO_2 from this reaction sequence. This oxidant source can be compared to others from the UWFPS data set, such as the Cl_2 fluxes determined above from industrial point sources, or with budgets inferred from the more comprehensive data sets associated with the ground-based measurements.

1.3.2 Halogens, Ozone and Oxidants

Ozone depletion associated with halogen species has been previously reported in Salt Lake City and attributed to natural sources of halogens from playa dusts followed by cycles such as reactions (R4-R6) [13]. The Twin Otter measurements from UWFPS confirm the phenomenon of ozone depletion associated with halogen compounds and provide a detailed set of spatially resolved chemical measurements to better understand it. As shown in Figure 3, these events were frequently observed on the west shore of the Great Salt Lake. The event in the figure occurred on the afternoon of January 16 and exhibited complete depletion of ozone associated with large mixing ratios of multiple halogen compounds, including HCl, shown in the figure. The event was confined to the region immediately adjacent to a single point source, although other observed events were more spatially widespread. Industrial activities in the region emit both halogens and nitrogen oxides, which also titrate ozone near emission sources through reaction with emitted NO.



The quantity $\text{O}_x = \text{O}_3 + \text{NO}_2$, commonly referred to as odd oxygen, is conserved in this reaction and accounts for the effect of NO_x titration on O_3 . As the Figure shows, O_x is nearly constant throughout the region at low altitudes (it is somewhat higher above 2 km above sea level, ASL) but depleted to zero in the region immediately adjacent to a large point source, eliminating the possibility that NO_x titration of O_3 is the cause of the ozone depletion event.

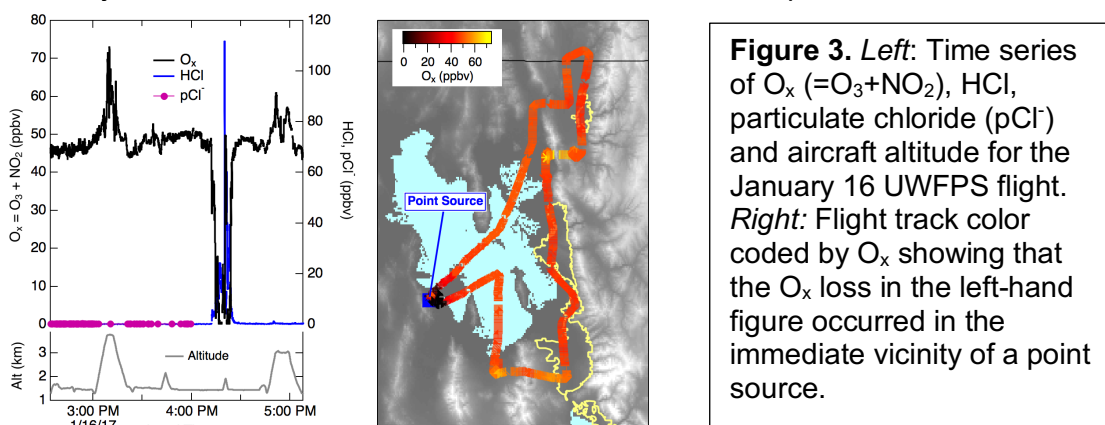


Figure 3. *Left:* Time series of O_x ($=\text{O}_3+\text{NO}_2$), HCl, particulate chloride (pCl) and aircraft altitude for the January 16 UWFPS flight. *Right:* Flight track color coded by O_x showing that the O_x loss in the left-hand figure occurred in the immediate vicinity of a point source.

This observation shows that at least this ozone depletion event is associated with an industrial rather than a natural halogen source. The observation also raises several research questions relevant to the impact of industrial halogen emissions on regional air quality. These questions and their associated analysis methods are outlined below.

Question 2: *Is the current understanding of the role of halogens in tropospheric chemistry consistent with the rates of ozone depletion and observed speciation of measured halogen species?*

Analysis Method: Chemical box modeling of halogen cycles and ozone depletion events

Aircraft observations of speciated halogens and ozone in industrial plumes during UWFPS provides an unprecedented opportunity to test the understanding of atmospheric halogen chemistry. Aircraft data from UWFPS provide observations of halogen – O_3 chemistry over a spatial domain of hundreds of meters to tens of kilometers downwind of the source, and a time

scale of minutes to hours. The data are also available during both daytime, when photolytic reactions of halogens are rapid, and night, when they should be inactive. Comparison of the predictions of a detailed chemical box model to these observations will provide an important test of fundamental understanding of the representation of halogens in chemical kinetic models.

Several research flights from UWFPS are suitable for this analysis. Figure 4 illustrates one example from a research flight on January 26, 2017. In this case, the aircraft followed the wind direction south over Stansbury Bay and eventually into the Tooele Valley. Similar to the example in Figure 3, O_x was approximately constant throughout the region except in the area where the presence of HCl marks the presence of halogen chemistry. The HCl is a marker for the endpoint in the chlorine chemistry since it is a stable product resulting from the reaction of atomic chlorine with methane or a VOC (R1). The observations from this flight provide a spectrum of transport distances and times in late afternoon. Levels of other halogens, such as Cl_2 , Br_2 , $BrCl$, $HOCl$ and $HOBr$ (not shown) were variable during this time as well and will provide useful model constraints.

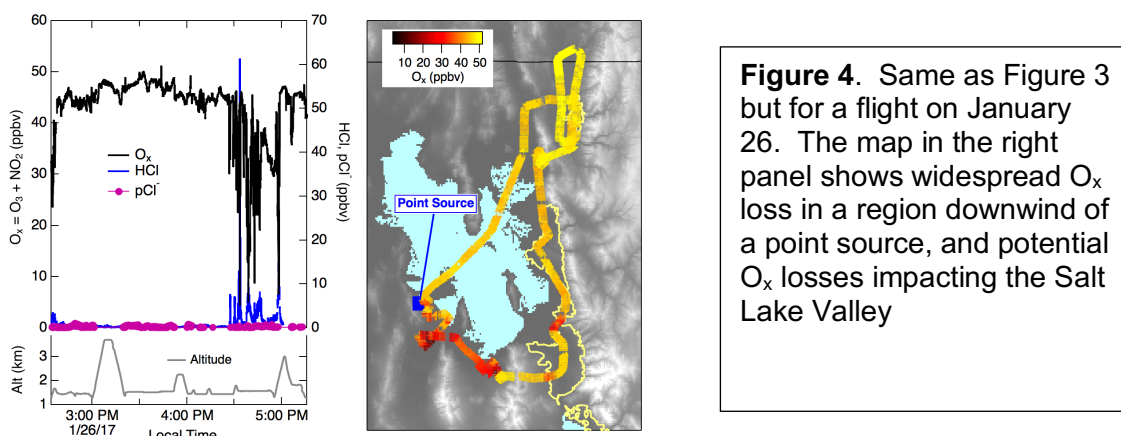


Figure 4. Same as Figure 3 but for a flight on January 26. The map in the right panel shows widespread O_x loss in a region downwind of a point source, and potential O_x losses impacting the Salt Lake Valley

A detailed chemical box model is a useful first step for comparison to these observations and similar flights. Such a box model requires a profile of speciated volatile organic compounds to model the combined effects of ozone depletion from the cycle in (R4-R6) and the influence of halogen radicals on HO_x - NO_x propagation cycles and ozone production. We have developed an urban VOC profile for the Salt Lake Valley based on three years of recent historical data with speciated VOC measurements from the Hawthorne monitoring site in the Salt Lake Valley [12]. The box model will take scaled VOC profiles from this work as inputs using tracers measured from the Twin Otter.

There are several potential modeling platforms that we are familiar with and that can be applied to this analysis. We have worked with the Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) [28] for several recent air quality modeling studies, including winter ozone in the Uintah Basin [29], summer ozone in the Colorado Front Range [30] and recently to model $PM_{2.5}$ in the Salt Lake Valley from UWFPS [12]. It is based on detailed chemistry provided by the Master Chemical Mechanism (MCM) [31], and in its recent implementation has used >2,500 species and >10,000 chemical reactions to model winter ozone in the Salt Lake Valley. The Framework for 0-D Atmospheric Modeling (F0AM) [32] is also a convenient model platform that we have recently implemented and that is also based on the MCM. In either case, we will either adapt the existing model chemical scheme to include an appropriate set of halogen reactions or take advantage of existing halogen modules that have already been developed for these models [21, 33].

Question 3: How does vertical and horizontal plume dispersion occur during transport across the Great Salt Lake, and how does this plume dispersion affect halogen chemistry.

Analysis Method: Plume dispersion modeling

Figure 5 shows a portion of the UWFPS January 28 flight over the Great Salt Lake in early evening. The aircraft profiled up and down over an altitude range of approximately 700 m, consistently locating an O₃ depleted, halogen containing plume within a relatively narrow altitude range. Data such as this can be combined with a plume dispersion model containing either an explicit or a simplified chemical scheme to understand the interaction between atmospheric chemistry and mixing, which is expected to be important in the case of background ozone mixing into a plume with active halogen depletion reactions.

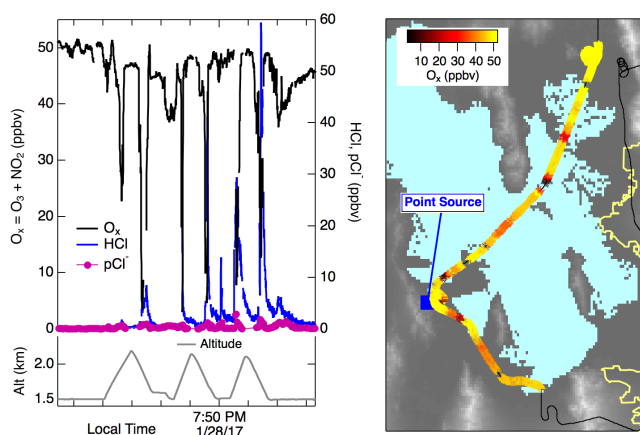


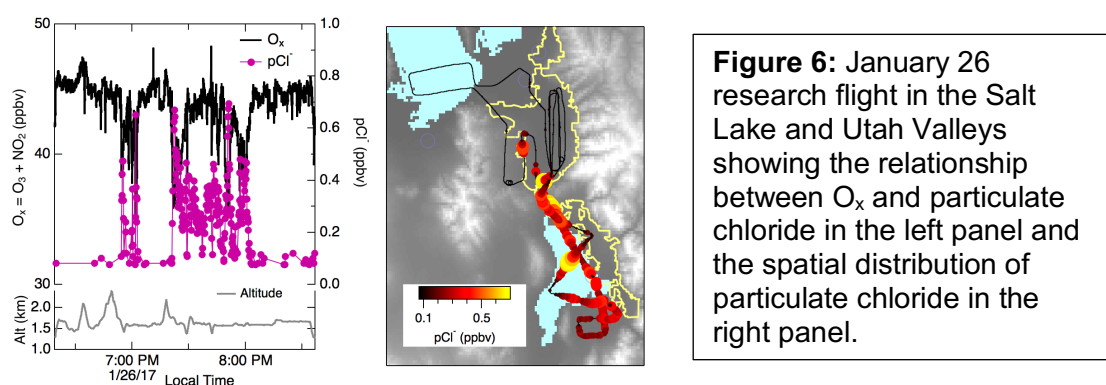
Figure 5: A portion of a research flight on January 28 showing halogens and O₃ depletions in a narrow vertical layer that is widespread in two different directions downwind of an industrial facility

We have previously worked with plume dispersion models to understand the nighttime chemistry of pollution plumes from coal-fired power plants [34-36]. In some cases, these models have used simplified chemical schemes, but more recently we have used a fully explicit chemical model [36]. A model has recently been developed at NOAA that combines plume dispersion with a detailed chemical scheme for interpretation of data from the recent FIREX-AQ airborne field study. Our previous studies have shown that rates of nitrogen oxide reactions are dependent on the degree to which background ozone mixes into a concentrated pollution plume. The same is likely true for halogen chemistry, although the relevant chemical mechanisms have not been analyzed in this context. Understanding this interaction will be an important second step towards characterizing the impact of industrial halogen emissions in the Great Salt Lake Basin. Figure 5 shows that the industrial plume can be widespread, dispersing into a discrete vertical layer that is found in two different directions from the source and across the entire domain of the Great Salt Lake, from the Bear Valley to the northeast to the Tooele Valley in the South.

Question 4: How widespread are the impacts of halogen depletion across the major valleys of the Great Salt Lake Basin, and how does this impact regional budgets for ozone and oxidants that are part of local PM_{2.5} production cycles. Is there evidence for ozone or oxidant production associated with inputs of halogen radicals?

Analysis Method: Assess the dependence of ozone and odd oxygen on halogen markers across the entire domain sampled by the Twin Otter during UWFPS.

Throughout the UWFPS data set, there are correlations between odd oxygen, defined above as $O_x = O_3 + NO_2$, and halogen markers, especially particulate chloride. In many cases particulate chloride is associated with reductions in O_x , while in others there may be weak positive correlations. Some of these correlations are clear indications of the effect of halogens on odd oxygen, as in the examples above, while others may be the result of simple covariance of multiple air pollutants. Figure 6 shows an example from the second research flight on January 26. The figure shows particulate chloride in mixing ratio units, but does not show HCl, which is below the instrument detection limit. Odd oxygen is negatively correlated with pCl⁻ in the boundary layer across the urban areas of the Salt Lake and Utah Valleys. Other reservoirs of odd oxygen, such as particulate nitrate [12, 37] are too small to account for the depletion. Relationships such as this in basins which do not contain industrial sources of halogens, but are adjacent to those that do may be indicative of a wider role for halogens in regulating the availability of oxidants, which is in turn important to the production rates for winter PM_{2.5}.



For this part of the analysis, relationships between different halogen markers, ozone and odd oxygen will be analyzed. The detailed chemical modeling above will be carried out across a range of NO_x , VOC and halogen levels to define the regimes under which halogens deplete O_3 or potentially contribute to its photochemical production.

1.4 Expected Outcomes

The influence of both natural and industrial halogen sources is important to modeling of winter PM_{2.5} in mountain valleys of northern Utah. The proposed analysis will provide quantitative estimates of anthropogenic halogen inputs in the Great Salt Lake basin, directly relevant to the improvement of emissions inventories. It will also provide process level information on the role of halogens in the production of oxidants, atmospheric radicals and PM_{2.5}. Finally, it will serve to improve understanding of PM_{2.5} chemical composition and sources.

1.5 Deliverables

The information from these two analyses will be prepared for publication in the peer-reviewed literature. We anticipate one paper for each major analysis topic (two in total), to be submitted to journals such as Atmospheric Chemistry and Physics, the Journal of Geophysical Research, the Journal of the Air and Waste Management Association or Atmospheric Environment. Computer code from any model development will be made available to UDAQ.

Preliminary results from these analyses will be presented at the Science for Solutions Conference in the spring of 2021.

1.6 Schedule

The schedule for the proposed work will involve two data analysis projects and will take place in the period July 1 2020 through June 30 2021. The table below gives an approximate timeline for the tasks. After a period of data quality assessment and assurance, the two analysis tasks will take place in parallel and on a time scale to allow presentation of results or a progress report at the Science for Solutions workshop in the spring of 2021 and submission of papers to peer reviewed journals within calendar year 2021.

	Q1 7/1 – 9/30 2020			Q2 10/1 - 12/31 2020			Q3 1/1 – 3/31 2021			Q4 4/1 – 6/30 2021		
Data collection and assessment of data quality												
Analysis 1: Halogen sources, speciation and partitioning												
Analysis 2: Influence of halogens on regional ozone												
Present results at Science for Solutions workshop												
Preparation of papers for submission to peer reviewed journals												

2. Budget

Table of proposed work effort for NOAA Participants

Name	Title	Person Months
Steven S. Brown	NOAA Federal Research Chemist	1*
Caroline C. Womack	CIRES Research Scientist II	6

*PI does not request salary support for the 1-month commitment

Funds are requested to support six months of salary for Dr. Caroline C. Womack, a Research Scientist with the Cooperative Institute for Research in Environmental Sciences (CIRES) at the University of Colorado (CU). Dr. Steven S. Brown, a federal civil servant and principal investigator, estimates a contribution of 1-person month, but no support is requested for this salary. Dr. Brown's salary is supported by NOAA as an in-kind contribution to the project.

Publication Charges

Funds are also requested for publication of two scientific papers at a cost of \$4000

Travel

Support is requested for travel for two investigators to attend the Science for Solutions workshop in Utah at a total cost of \$1402 (Airfare = \$500, hotels = \$508, meals = \$244, rental

car = \$150). Expenses have been calculated using standard U.S. government per-diem rates.

Detailed Budget

DIRECT COSTS

SALARIES	Monthly Rate	FTE or % Effort	Number of Months	Total Cost
A. PI Dr. Steven Brown (Federal civil servant)	\$ -	100.0%	2.00	\$ -
B. Co-I Dr. Caroline Womack (CIRES Scientist II)	\$ 7,500	100.0%	6.00	\$ 45,000
SUBTOTAL - SALARIES				\$ 45,000
Benefits rate set by CU/CIRES	36.40%			\$ 16,380
Travel - 2 person-trips to Salt Lake City, UT				\$ 1,402
Publication - 1 manuscript submitted for peer review				\$ 4,000
TOTAL DIRECT COSTS				\$ 66,782
Overhead rate set by CU/CIRES	20.00%			\$ 12,556
Task 1 fee set by CU/CIRES	2.20%			\$ 1,657
Admin fee set by CSD Director's Office	3.00%			\$ 2,430
TOTAL INDIRECT COSTS				\$ 16,644
TOTAL				\$ 83,426

3. Personnel Roles and Responsibilities

The principal investigator, Dr. Steven Brown, will review the relevant data from the UWFPS campaign at the project outset. He will be responsible for quality control of analysis results and editing of publications submitted for peer review and for drafting and submitting interim and final reports. Dr. Caroline Womack will conduct the analyses of halogen sources, gas-particle partitioning and contribution to the radical budget as detailed in the scope of work. She will analyze the data collected aboard the Twin Otter primarily, but will also utilize data from ground sites during the UWFPS campaign as necessary. She will further be responsible for the analysis of halogens and their impact on regional ozone and oxidants in the Great Salt Lake basin. She will analyze the data from UWFPS and run appropriate box models or plume dispersion models. She will prepare a manuscript for review of relevant co-authors to be submitted as a peer reviewed publication. She will then draft and submit a relevant manuscript containing the results of this work.

Both investigators have been involved with the UWFPS project from the beginning and already have familiarity with the dataset and instrumentation involved, and the chemical processes and box modeling methods proposed here.

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